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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>5</sup> :</b> <b>C11D 7/16, 7/32, 7/36</b> <b>C11D 7/50</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/15178</b> <b>(43) International Publication Date:</b> 5 August 1993 (05.08.93)
<b>(21) International Application Number:</b> PCT/US93/00953 <b>(22) International Filing Date:</b> 3 February 1993 (03.02.93)  <b>(30) Priority data:</b> 07/829,357 3 February 1992 (03.02.92) US 07/964,613 22 October 1992 (22.10.92) US  <b>(71) Applicant:</b> MOTSENBOCKER ADVANCED DEVELOPMENT, INC. [US/US]; 87 Felspar Street, San Diego, CA 92109 (US). <b>(72) Inventor:</b> MOTSENBOCKER, Gregg, A. ; P.O. Box 5857, Blue Jay, CA 92317 (US). <b>(74) Agent:</b> WELCH*, Edward, K., II; Loctite Corporation, Hartford Square North, 10 Columbus Boulevard, Hartford, CT 06106-5108 (US).		<b>(81) Designated States:</b> AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> AQUEOUS CLEANER CONTAINING TRISODIUM PHOSPHATE, EDTA OR PHYTIC ACID, AND SOLVENT MIXTURE  <b>(57) Abstract</b>  Water-based cleaning compositions for removing a variety of stains or deposits from a variety of substrates, the compositions consisting essentially of tri-sodium phosphate; ethylene diamine tetra acetic acid (EDTA) and/or phytic acid or a mixture of them; ethylene n-butyl ether and/or butyl salicylate or a mixture of them; and acetone and/or a member of the group consisting of dimethyl adipate, dimethyl glutarate, dimethyl succinate or a mixture of them in water. Such compositions may further contain acetic acid, hydrogen peroxide or both.		

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**TITLE OF THE INVENTION**

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Aqueous Cleaner Containing Trisodium Phosphate, Edta or Phytic Acid, and Solvent Mixture

10 **FIELD OF THE INVENTION**

Cleaning compositions to remove from surfaces such as carpets, cloth, hard surfaces, leather and suede, deleterious deposits and stains so as to restore them as closely as possible to a clean  
15 condition.

**BACKGROUND OF THE INVENTION**

20 Porous surfaces, such as those of carpets, clothing, table-cloths, napkins, automobile seats, athletic shoes, leather, suede, and certain metal and metal composites, to name only few, and hard surfaces such as concrete, stucco, metal signs, tile, wallpaper and wood floors, often receive deleterious deposits, stains, and  
25 graffiti. Such deposits vary widely in their identity. Some may be quite viscous, for example paints, greases, and sauces such as mustard, ketchup, and mayonnaise. Others are more liquid in nature, such as pet stains, wines, soft drinks, ball point inks, marker inks, fountain pen inks, and printers inks. Still others may be  
30 more solid or pasty, including foods, especially proteinaceous foods, water-based adhesives, and latex-based paints.

Some types of hard surfaces often have deposits respective to their storage and preservation. Examples are oily compositions to

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protect them from corrosion, residues from cutting oils for which a degreaser is usually needed, and dust on disc brakes which must be removed.

5 The above recitation exemplifies a broad range of materials which need to be cleaned of a broad range of deposits and stains. In response to this need, an equally wide range of cleaning compositions already exists in the market.

10 Generally speaking, however, commercial compositions are limited both in the range of their effectiveness and also as to how efficient they really are for their intended purpose. Consequently, if one intends to remove a wide range of kinds of deposits or stains, one is likely to find a nearly-equal number of formulations to buy for that purpose, each somewhat specific for a given deposit or stain. Even then, some of the stains and deposits are usually  
15 only partially removed. Furthermore, many of the commercial compositions pose a significant risk to the material being cleaned, for example, they may discolor the material or may attack the material itself. In spite of the numerous cleaning compositions available in the consumer market today, there is no known composition  
20 tion which will remove marking pen dye from a white tablecloth, let alone any number of additional deposits and stains. Yet, surprisingly, compositions according to the present invention will.

Furthermore, many existing cleaning and stain removal compositions are objectionable from an environmental standpoint, employing  
25 large amounts of volatile and/or organic solvents. Unlike the commercial materials, compositions according to the invention are water-based and generally environmentally acceptable.

It is an object of this invention to provide a water-based, environmentally acceptable, essentially biodegradable cleaning  
30 composition which can be used to remove a surprisingly wide range of types of deposits and stains. It is also an object of the present invention to provide a cleaning composition which, itself or any residues, will not harm the user nor the surfaces to which it is applied. It is surprising to observe how many types of really  
35 difficult stains and deposits these compositions can remove with

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little or no remaining evidence that there ever had been a stain or a deposit or that the substrate had been treated with a cleaning composition.

It is another object to provide a small family of related compositions, each with somewhat different concentrations of essentially the same ingredients, although some variation of constituents is allowed as described herein, which between them can attend to all but a few of the types of deposits and stains which predictably will be experienced. Indeed, it is surprising to find that as few as two or three such related individual formulations will provide nearly optimum removal of a very broad assortment of deposits.

#### BRIEF DESCRIPTION OF THE INVENTION

A composition according to this invention which provides for a wide range of applications is water-based and comprises, in addition to water: tri-sodium phosphate; ethylene diamine tetra acetic acid (EDTA) and/or phytic acid or a mixture of them; ethylene n-butyl ether and/or butyl salicylate or a mixture of them; and acetone and/or a member of the group consisting of dimethyl adipate, dimethyl glutarate, dimethyl succinate or a mixture of them. Such compositions are surprisingly effective for the removal of beverage stains, pet stains, food stains and deposits, latex-based paints, proteins, dust and corrosion preservatives.

The range and speed of effectiveness of this composition can be greatly extended by the further addition of hydrogen peroxide. When this is added, fluid inks, marker inks, and ball point inks, are better removed at faster speeds, and often decolorized, which for clothing achieves the desired stain removal.

According to an optional feature of the invention, the hydrogen peroxide is added to the basic formulation either at the time of packaging, or at the time of application, which provides for valuable improvement of performance on certain stains and deposits. When provided at the time of application, shelf life is improved.

According to yet another optional feature of the invention, dis-

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coloring of the composition may largely be avoided by replacing some of the formulation with a minor amount of acetic acid, thereby increasing the attractiveness of the product and thereby extending its salable shelf life.

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#### DETAILED DESCRIPTION OF THE INVENTION

This product consists essentially of a member of each of the following groups of ingredients:

- 10 a. trisodium phosphate (TSP);
- b. ethylene diamine tetra acetic acid (EDTA), phytic acid, or a mixture of the two;
- c. ethylene glycol n-butyl ether (Glycol EB), butyl salicylate, or a mixture of the two;
- 15 d. acetone or a dibasic ester selected from the group consisting of dimethyl adipate, dimethyl glutarate, and dimethyl succinate, or a mixture of the dibasic esters with or without acetone; and
- e. water.

- 20 The proportions of the member or members in each group in the ultimate product are in part determined by the application for which the product is intended. There is a surprising versatility and synergy in this combination of constituents. Variations within defined ranges will in every case provide some useful cleaning
- 25 operation. Depending on the targeted deposits and stains as well as the substrates from which the deposit or stain is to be removed, remarkable improvements can be secured by varying the relative proportions of the constituents, and, when appropriate, using one constituent in a group instead of, or along with, another in that
- 30 same group.

- For example, there is an economically targeted first group of stains and deposits that are likely to be encountered on clothing, carpets and furniture which have a water or a protein base. These occur principally as the consequence of inadvertencies of people and
- 35 household pets who spill or slop things. Exemplary of such stains

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and deposits there may be given beverage stains such as fruit juices, coffee, tea, Kool Aid<sup>R</sup> drinks (a particularly difficult stain for conventional cleaners), red wine, liquor, and milk; yogurt; condiments such as ketchup, mustard, mayonnaise, and spaghetti sauces; and various other substances such as chocolate, vomit, urine, feces, blood, grass stains, pet stains, berry stains, dirt, Play Doh<sup>R</sup> modeling clay, and perspiration.

Removal of these targeted substances, especially when on cloth substrates, is favored by providing a somewhat lesser percentage of groups (a), (c), and (d) and a somewhat larger percentage of groups (b) and (e).

A second class of stains and deposits to be removed include those which are not generally amenable to removal with many or even most water-based cleaners, even though they may be somewhat soluble or releasable in water. Generally, these stains and deposits derive from substances which typically contain or had contained organic solvents. Examples of this second group of substances are inks from writing and marking instruments, newsprint, paints, hi-liters, nail polish, staining agents, and dyes. They are often encountered on walls, metal signs, varnish and lacquer surfaces, tire sidewalls, automotive brake discs, metal parts, and tennis shoes, for example.

In accordance with the present invention, these types of stains and deposits are best removed by a cleaner with a relatively higher concentration of groups (a), (c), and (d), and a relatively lower concentration of groups (b) and (e).

While both of the aforementioned classes of stains and deposits may be found on any number of kinds or varieties of substrates, the first group of stains and deposits, as well as inks and marker stains from the second class, are generally found on substrates which are more delicate in character and composition. A specific example of such substrates are cloth substrates or fabrics typically found around the house (i.e., furniture coverings, tablecloths, curtains, carpeting, etc.), as well as wearing apparel. It is interesting to observe that formulations appropriate for removing such stains and deposits from these substrates are generally

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sufficiently dilute that they do no harm to most such substrates. In fact, in many situations it is not even necessary to rinse them off, although this will usually be the best practice.

As to the second class of stains and deposits, they are more likely to be found on solid and more substantial substrates, for example, walls, woodwork, signs, etc. In these cases, higher concentrations of active constituents will preferably be used. Additionally, it is more likely, and recommended, that attention be given to rinsing off the cleaner and the material it releases. In general, the cleaner used for these applications will be thought of as being "stronger" in character.

In all cases, the cleaner can be supplied as a liquid and, if desired and feasible, the substrate could be submerged in the cleaner. In some situations, especially on porous substrates such as concrete, stucco or brick from which graffiti is to be removed, it may instead be sprayed on or be applied as an aerosol.

Compositions of the type contemplated by this invention tend to become cloudy unless steps are taken to avoid it. Although the cloudy solution is still as effective as the clear solution, it may be less attractive to a potential purchaser. Thus, it has been found that cloudiness can largely be avoided by using di-ionized water in the formulation and by dissolving certain constituents in a portion of the water prior to adding it to the remainder of the formulation.

It has also been found that the removal of some stains and deposits is improved by the inclusion of hydrogen peroxide in the formulation. This is particularly helpful in the removal of certain inks and paints; marker pen ink, for example. When hydrogen peroxide is to be employed, it is simply added to the formulation as previously specified. Consequently, the proportions of the required constituents, one to another, will not change. Thus for a given amount of the cleaning composition, the amount of hydrogen peroxide to be employed will simply replace an equal amount of the base formulation.

Under some circumstances, and in some ranges of concentrations, the formulation over time shows a tendency to discolor. While the



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cleaning capacity remains good, the product is less attractive to a purchaser, thereby reducing its shelf life in the store. This tendency can largely be overcome by the addition of a minor amount of acetic acid to the solution. In specifying the addition of acetic acid, the same considerations are used for specifying proportions as described above for when the hydrogen peroxide is added.

The cleaning compositions according to this invention are water-based products. Percentages specified herein are in weight percentage of the total composition. In preparing the formulations of the present invention, it is possible to add all of the ingredients to the water at one time; however, a cloudy solution may result. Generally, it is preferred to dissolve/add certain of the ingredients into a portion of the water before adding them into the total formulation. This will most often assure the formation of a clear product. For example, it is preferred practice to dissolve the TSP in a portion of the water before adding the other ingredients. In this regard, a TSP:water ratio (again by weight) of between about 1:12 to about 1:40, preferably from about 1:12 to 1:20, and, most preferably, about 1:20, is suitable. Similarly, EDTA is best supplied not as a dry product, but in a diluted form; for example, about 34% EDTA to about 66% water. Dilute EDTA is readily available in industrial concentrations from numerous suppliers.

The other ingredients are either already liquid or readily dissolved so as to enter the solution or be miscible with it. No special procedure is necessary as to them.

There is no criticality with respect to the water to be used in making the foregoing solutions or for rounding out the overall formulation. However, in order to avoid cloudiness of the formulation, it is preferred to use purified water (e.g., distilled, de-ionized or softened), especially di-ionized water.

In all the formulations and guidelines given below, at least one substance from each group must be included. All of the constituents to be used in the formulations of the present invention are commercially available. Certain of the preferred constituents and the nature in which they are to be employed are as follows:

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TSP [trisodium phosphate] - CAS No. 101-89-0

EDTA [ethylene diamine tetra acetic acid (industrial grade 34%  
EDTA in water)] - CAS No. 64-02-8

5 glycol EB [ethylene glycol mono n-butyl ether (2 butoxy  
ethanol)] - CAS No. 111-76-2

acetone - CAS No. 67-64-1

glacial acetic acid - CAS No. 64-19-17

de-ionized water

10 The following sets forth various formulations which may be  
prepared in accordance with the present invention. All amounts are  
expressed in terms of % by weight.

General Formulation:

- a. trisodium phosphate, between about 0.85% and about 3.5%;
- b. ethylene diamine tetra acetic acid (EDTA) or phytic acid, or a  
15 mixture of them, between about 0.9% and about 9.0%;
- c. ethylene glycol n-butyl ether, or butyl salicylate, or a  
mixture of them, between about 2.27% and about 27.0%;
- d. acetone or a dibasic ester or esters selected from the group  
consisting of dimethyl adipate, dimethyl glutarate, and dimethyl  
20 succinate, or a mixture of such dibasic esters, with or without  
acetone, between about 2.0% and about 18.0%; and
- e. water to make 100%.

Preferred General Use Formulation:

- a. trisodium phosphate, about 1.75%;
- 25 b. ethylene diamine tetra acetic acid (EDTA) or phytic acid, or a  
mixture of them, about 9.0%;
- c. ethylene glycol n-butyl ether, or butyl salicylate, or a mixture  
of them, about 15.4%;
- d. acetone or a dibasic ester or esters selected from the group  
consisting of dimethyl adipate, dimethyl glutarate, and dimethyl  
30 succinate, or a mixture of such dibasic esters, with or without  
acetone, about 6.3%; and
- e. water to make 100%.

Preferred Modified Formulation for Certain Deposits:

- 35 a. trisodium phosphate, about 2.1%;

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- b. ethylene diamine tetra acetic acid (EDTA) or phytic acid, or a mixture of them, about 4.5%;
- c. ethylene glycol n-butyl ether, or butyl salicylate, or a mixture of them, about 18.1%;
- 5 d. acetone or a dibasic ester or esters selected from the group consisting of dimethyl adipate, dimethyl glutarate, and dimethyl succinate, or a mixture of such dibasic esters, with or without acetone, about 8.2%; and
- e. water to make 100%.

10 Especially preferred embodiments of the above formulations employ, as indicated previously, the following commercial materials; tri-sodium phosphate, industrial grade EDTA, glycol EB, and acetone in the amounts specified. In preparing the foregoing formulations the TSP was first dissolved in de-ionized water in a weight ratio of  
15 1:20 TSP:water.

As mentioned previously, acetic acid may be added to the foregoing formulations to retard or prevent discoloring of the cleaning composition. When used, it is preferred to use glacial acetic acid. Generally, the amount of acetic acid to be used will  
20 be minor in order to obtain the benefit mentioned, most notably about one once for every 21 ounces of the formulation.

When hydrogen peroxide is to be employed in the practice of the present invention, it is preferred to use it as a dilute solution in strengths of between about 1% and about 5%  $H_2O_2$  in water. The  
25 amount of be used will be a minor amount, essentially that which will enhance cleaning performance of certain difficult to remove stains and deposits as noted previously. Generally, the hydrogen peroxide solution will comprise from about 15% to about 30%, most preferably about 20%, of the overall cleaning composition. While  
30 the hydrogen peroxide solution can be added to the formulation itself, and sold as such, it will be better practice to apply it separately, at the time of use, in these proportions. This can be accomplished by mixing the hydrogen peroxide solution and the cleaning formulation in a container, or by mixing in a spray or  
35 mixing device which will combine a stream of hydrogen peroxide and

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the cleaner just prior to, at the time of or just after application of one or the other to the substrate. A longer shelf life of the product can be anticipated if the cleaner and hydrogen peroxide are kept separate until they are used.

5       The specific selection of the various components of the cleaning formulation will largely be decided on the basis of economics and, to some extent, the type of stain, etc. to be removed. Nevertheless, all of them are useful in the cleaner and it is a matter of preference whether to use one or another.

10       Trisodium phosphate is a well-known cleaning composition. However, in many regions its usage is severely restricted by environmental laws and regulations. It is an advantage to this invention that, due to the low concentrations used in this invention, particularly the lower end concentrations, it is acceptable under the  
15       most stringent existing laws and regulations. Still, with the other components it provides a very effective cleaning composition.

      The combination of components used herein appears to function synergistically, by mechanisms which are not fully understood at this time. In general, the formulations of the present invention have a  
20       degree of effectiveness much greater than compositions already known for the intended purposes.

      Formulations according to this invention are remarkably versatile and effective for a wide range of deposits and stains on a wide range of substrates. Any residues can readily be removed by simple  
25       washing or rinsing with water or laundering of the substrate that a clean surface remains.

      This invention is not to be limited by the embodiment described in the description, which is given by way of example and not limitation. Various alternative embodiments and modifications to the  
30       formulations specified above can be devised by those skilled in the art, in view of the present teaching, without departing from the invention. Accordingly, the present invention is intended to embrace all such alternative embodiments and modifications which fall within the scope of the appended claims.

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## I CLAIM:

1. A cleaner for removing deleterious deposits and stains from a substrate characterized in that it comprises a solution consisting essentially of at least one member selected from each of the following groups:
- a. trisodium phosphate (TSP);
  - b. ethylene diamine tetra acetic acid (EDTA), phytic acid, or a mixture of the two;
  - c. ethylene glycol n-butyl ether (Glycol EB), or butyl salicylate, or a mixture of the two;
  - d. acetone or a dibasic ester selected from the group consisting of dimethyl adipate, dimethyl glutarate, and dimethyl succinate, or a mixture of such dibasic esters with or without acetone; and
  - e. water
- in such relative proportions as to provide a free flowing aqueous solution effective to remove said deposits and stains from said substrates.
2. A cleaner for removing deleterious deposits and stains from a substrate characterized in that it comprises, as a weight percent of the entire formulation:
- a. trisodium phosphate, between about 0.85% and about 3.5%;
  - b. ethylene diamine tetra acetic acid (EDTA), phytic acid, or a mixture of the two, between about 0.9% and about 9.0%;
  - c. ethylene glycol n-butyl ether (Glycol EB), or butyl salicylate, or a mixture of the two, between about 2.27% and about 27.0%;
  - d. acetone or a dibasic ester selected from the group consisting of dimethyl adipate, dimethyl glutarate, and dimethyl succinate, or a mixture of such dibasic esters with or without acetone, between about 2.0% and about 18.0%; and
  - e. water to make 100%.

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3. A cleaner for removing deleterious deposits from a substrate characterized in that it comprises, as a weight percentage of the entire formulation:
- a. trisodium phosphate, about 1.75%;
  - 5 b. ethylene diamine tetra acetic acid (EDTA), phytic acid, or a mixture of them, about 9.0%;
  - c. ethylene glycol n-butyl ether (Glycol EB), or butyl salicylate, or a mixture of them, about 15.4%;
  - 10 d. acetone or a dibasic ester selected from the group consisting of dimethyl adipate, dimethyl glutarate, and dimethyl succinate, or a mixture of such dibasic esters with or without acetone, about 6.3%; and
  - e. water to make 100%.
- 15 4. A cleaner for removing deleterious deposits from a substrate characterized in that it comprises: as a weight percentage of the entire formulation:
- a. trisodium phosphate, about 2.1%;
  - 20 b. ethylene diamine tetra acetic acid (EDTA), phytic acid, or a mixture of them, about 4.5%;
  - c. ethylene glycol n-butyl ether (Glycol EB), or butyl salicylate, or a mixture of them, about 18.1%;
  - d. acetone or a dibasic ester selected from the group consisting of dimethyl adipate, dimethyl glutarate, and dimethyl succinate, or a mixture of such dibasic esters with or without acetone, about 8.2%; and
  - 25 e. water to make 100%.
- 30 5. A cleaner according to claim 1, 2, 3, or 4 wherein component (b) is EDTA, component (c) is Glycol EB, and component (d) is acetone.
6. A cleaner according to claim 5 wherein the EDTA is industrial grade EDTA.

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7. A cleaner according to claim 1, 2, 3, or 4 which further includes a minor amount of acetic acid.
8. A cleaner according to claim 7 in which the acetic acid is present in an amount of about one once for each 21 ounces of the formulation of components (a), (b), (c), (d), and (e).
9. A cleaner according to claim 1, 2, 3, or 4 which further includes a minor amount of hydrogen peroxide.
10. A cleaner according to claim 9 in which the hydrogen peroxide is a solution of about 1% to about 5%  $H_2O_2$  in water.
11. A cleaner according to claim 10 in which the hydrogen peroxide is present in an amount of between 15% and 30% by weight of the overall formulation.
12. A cleaner according to claim 10 in which the hydrogen peroxide solution comprises about 20% by weight of the overall formulation.
13. A cleaner according to claim 9 in which the hydrogen peroxide is added to the formulation.
14. A cleaner according to claim 9 in which the hydrogen peroxide is to be combined with the formulation at the time it is applied to the substrate to be cleaned.
15. A cleaner according to claim 9 which further includes a minor amount of acetic acid.
16. A cleaner according to claim 15 in which the acetic acid is present in an amount of about one once for each 21 ounces of the formulation of components (a), (b), (c), (d), and (e).

SUBSTITUTE SHEET

## INTERNATIONAL SEARCH REPORT

PCT/US93/00953

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C11D 7/16, 7/32, 7/36, 7/50

US CL : 252/104, 135, 139, 153, 173, 174.16, 527

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/170

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,607,760 (MCINTYRE) 21 SEPTEMBER 1971 SEE THE EXAMPLE AND CLAIMS	1
Y	US, A, 4,242,217 (Westermann) 30 December 1980, See column 2, lines 5 and 67 and example 1.	1
Y	US, A, 3,822,212 (Bryant) 02 July 1974, See the claims.	1
Y	US, A, 4,485,028 (King) 27 November 1984, See the examples.	1
Y	US, A, 4,774,015 (Slover) 27 September 1988, See the claims.	1
Y	US, A, 3,950,277 (Stewart) 13 April 1976, See column 6, lines 46 and 56.	1

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

24 MARCH 1993

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/00953

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,780,235 (JACKSON) 25 OCTOBER 1988 SEE COL. 2, LINES 5-20 AND 38	1
Y	US,A, 4,927,556 (POKORNY) 22 MAY1990 SEE THE CLAIMS	1